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(54) Title: LAMINATE STRUCTURES FOR FUEL CONTAINERS

(57) Abstract

A multilayer laminate structure comprising (A) one or more layers of a polyolefin or a blend of two or more different polyolefins; and (B) one or more layers of a fuel barrier polymer or blends thereof, the fuel barrier polymer or blends thereof having a Fuel CM15 permeability of 45 g-mil/m^2-day or less, based on a layer thickness of 1 mil, when measured at 40 °C and under ambient pressure conditions of 700 to 760 torr; and optionally (C) a tie layer interposed between a polyolefin layer and an adjacent fuel barrier layer; and/or optionally (D) a regrind layer interposed between a tie layer and a polyolefin layer.

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LAMINATE STRUCTURES FOR FUEL CONTAINERS

This invention relates to multilayer laminate structures having barrier properties (permeation preventing properties) with respect to vehicle fuels (such as gasoline) and mixtures of hydrocarbons with oxygen-containing organic compounds (such as gasoline containing alcohol compounds).

Fuel tanks made of a multilayer laminate material comprising a layer of a particular polyethylene, a barrier layer made of a polyester, such as polyethylene terephthalate (PET), and an adhesive layer made of a modified polyethylene are described in U.S. Patent 5,443,874. However, PET is swelled significantly by oxygenated fuels, especially fuels in which the oxygenate is an alcohol such as methanol, and therefore, is a poor barrier to oxygenated fuels. Ethylene vinyl alcohols (EVOH), such as Eval™ F, a product of Eval Co., are currently used as fuel barriers in the manufacture of fuel tanks. However, Eval F, as known in the automotive industry, does not provide adequate barrier properties toward oxygenated fuels in which the oxygenate is an alcohol, such as methanol. In addition, Eval F is known to the packaging industry to be moisture sensitive, which, after exposure to moisture, possesses a substantially higher rate of permeation of oxygen, carbon dioxide, water vapor, and volatile organic compounds through films of this material.

Multilayer containers comprising an inner layer of poly(ethylene naphthalenedicarboxylate) and an outer layer of poly(ethylene terephthalate) are described in U.S. Patent 5,443,766. This structure, is too expensive for the fuel tank application.

It would be desirable to provide a multilayer laminate structure for making containers for vehicle fuels and mixtures of hydrocarbons with oxygen-containing organic compounds which do not have the above disadvantages of the prior art structures.

In a first aspect, the present invention is a multilayer laminate structure comprising:

(A) one or more layers of a polyolefin or a blend of two or more different polyolefins; and

(B) one or more layers of a fuel barrier polymer or blends thereof selected from:

(1) a hydroxy-functionalized polyether containing an α-alkylstilbene moiety,

(2) a polyester containing an α-alkylstilbene moiety,

(3) a polycarbonate containing an α-alkylstilbene moiety,

(4) polyester-co-carbonate containing an α-alkylstilbene moiety,

(5) polyacetal,

(6) blends of (1), (2), (3), (4), (5), and/or a thermoplastic polyester, and/or a toughening agent and/or a filler having a high aspect ratio, and

(7) a blend of (a) poly(butylene terephthalate) (PBT), (b) poly(ethylene terephthalate)(PET), and/or (c) a toughening agent and/or (d) a filler having a high aspect ratio; and, optionally

(C) a tie layer interposed between a polyolefin layer and an adjacent fuel barrier layer; and/or optionally

(D) a regrind layer interposed between a tie layer and a polyolefin layer.

In a second aspect, the present invention is a multilayer laminate structure comprising:

(A) an outer layer of a polyolefin or a blend of two or more different polyolefins; and

(B) an inner layer of a fuel barrier polymer or blends thereof, the fuel barrier polymer or blends thereof having a Fuel CM15 permeability of 45 g-mil/m^2-day or less, based on a layer thickness of 1 mil, when measured at 40°C and under ambient pressure conditions of 700 to 760 torr; and optionally

(C) a tie layer interposed between a polyolefin layer and an adjacent fuel barrier layer; and/or optionally

(D) a regrind layer interposed between a tie layer and a polyolefin layer.

In a third aspect, the present invention is a multilayer laminate structure comprising:

(A) an inner layer of a fuel barrier polymer, and/or

(B) an outer layer of a fuel barrier polymer,

the fuel barrier polymer selected from:

(1) a hydroxy-functionalized polyether containing an α-alkylstilbene moiety,

(2) a polyester containing an α-alkylstilbene moiety

(3) a polycarbonate containing an α-alkylstilbene moiety,

(4) a polyester-co-carbonate containing an α-alkylstilbene moiety,

(5) poly(ethylene-2,6-naphthalenedicarboxylate) (PEN),

(6) poly(butylene-2,6-naphthalenedicarboxylate) (PBN),

(7) poly(butylene terephthalate) (PBT),

(8) poly(propane terephthalate) (PPT),

(9) polyacetal, and

(10) blends of (1), (2), (3), (4), (5), (6), (7), (8), and/or (9), and/or PET, and/or a toughening agent and/or a filler having a high aspect ratio; and

(C) a core layer of a polyolefin or a blend of two or more different polyolefins; and optionally

(D) a tie layer interposed between a polyolefin layer and an adjacent fuel barrier layer; and/or optionally

(E) a regrind layer interposed between a tie layer and a polyolefin layer.

In a fourth aspect, the present invention is a multilayer laminate structure comprising:

(A) an inner layer and an outer layer of a polyolefin or a blend of two or more different polyolefins,

(B) a core layer of a fuel barrier polymer consisting of a blend of EVOH and a filler having a high aspect ratio; and optionally

(C) a tie layer interposed between a polyolefin layer and an adjacent fuel barrier layer; and/or optionally

(D) a regrind layer interposed between a tie layer and a polyolefin layer.

In a fifth aspect, the present invention is a process for preparing the multilayer laminate structures of the first, second, third and fourth aspects, which comprises coextruding the layers defined in each of said aspects.

When formed into a container, the inner layer of the multilayer laminate structure is the layer which comes in contact with the fuel placed inside the container.

As used herein, the term "Fuel CM15" refers to a test fuel mixture consisting of 42.5 volume percent toluene, 42.5 volume percent isooctane and 15 volume percent methanol. The multilayer laminate structure of the present invention can be used wherever very good fuel resistance and hydrolytic stability is desired. Hence, the multilayer laminate structure can be used as a container, such as a fuel tank for any vehicle, for example, a jet aircraft, an automobile, truck, lawn and garden applications; marine applications; and storage tanks or bottles for chemicals. The laminate structure can also be used as tubing for the transfer of fuel or chemicals.

By the term "polyolefin" is meant a polymer or copolymer of ethylene, that is, a polymer derived solely from ethylene, or ethylene and one or more monomers copolymerizable therewith. Such polymers (including raw materials, their proportions, polymerization temperatures, catalysts and other conditions) are well-known in the art and reference is made thereto for the purpose of this invention. Additional comonomers which can be polymerized with ethylene include olefin monomers having from 3 to 12 carbon atoms, ethylenically unsaturated carboxylic acids (both mono- and difunctional) and derivatives of such acids such as esters (for example., alkyl acrylates) and anhydrides; monovinylidene aromatics and monovinylidene aromatics substituted with a moiety other than halogen such as styrene and methylstyrene; and carbon monoxide. Exemplary monomers which can be polymerized with ethylene include 1-octene, acrylic acid, methacrylic acid, vinyl acetate and maleic anhydride.

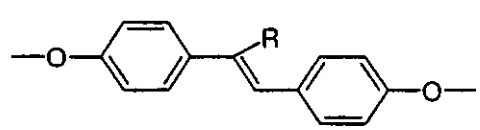
Polyolefins which can be employed in the practice of the present invention for preparing the multilayer laminate structure include polypropylene, polyethylene, and copolymers and blends thereof, as well as ethylene-propylene-diene terpolymers. Preferred polyolefins are polypropylene, linear high density polyethylene (HDPE), heterogeneously-branched linear low density polyethylene (LLDPE) such as DOWLEX™ polyethylene resin (a trademark of The Dow Chemical Company), heterogeneously branched ultra low linear density polyethylene (ULDPE) such as ATTANE™ ULDPE (a trademark of The Dow Chemical Company); homogeneously-branched, linear ethylene/α-olefin copolymers such as TAFMER™ (a trademark of Mitsui Petrochemicals Company Limited) and EXACT™ (a trademark of Exxon Chemical Company); homogeneously branched, substantially linear ethylene/α-olefin polymers such as AFFINITY™ (a trademark of The Dow Chemical Company) and ENGAGE® (a trademark DuPont Dow Elastomers L.L. C) of polyolefin elastomers, which can be prepared as disclosed in U.S. Patents 5,272,236 and 5,278,272; and high pressure, free radical polymerized ethylene polymers and copolymers such as low density polyethylene (LDPE), ethylene-acrylic

acid (EAA) copolymers such as PRIMACOR™ (trademark of The Dow Chemical Company), and ethylene-vinyl acetate (EVA) copolymers such as ESCORENE™ polymers (a trademark of Exxon Chemical Company), and ELVAX™ (a trademark of E.I. du Pont de Nemours & Co.). The more preferred polyolefins are the homogeneously-branched linear and substantially linear ethylene copolymers with a density (measured in accordance with ASTM D-792) of 0.85 to 0.99 g/cm^3, a weight average molecular weight to number average molecular weight ratio (Mw/Mn) from 1.5 to 3.0, a measured melt index (measured in accordance with ASTM D-1238 (190/2.16)) of 0.01 to 100 g/10 min, and an I10/I2 of 6 to 20 (measured in accordance with ASTM D-1238 (190/10)).

In general, high density polyethylene (HDPE) has a density of at least about 0.94 grams per cubic centimeter (g/cc) (ASTM Test Method D-1505). HDPE is commonly produced using techniques similar to the preparation of linear low density polyethylenes. Such techniques are described in U.S. Patents 2,825,721; 2,993,876; 3,250,825 and 4,204,050. The preferred HDPE employed in the practice of the present invention has a density of from 0.94 to 0.99 g/cc and a melt index of from 0.01 to 35 grams per 10 minutes as determined by ASTM Test Method D-1238.

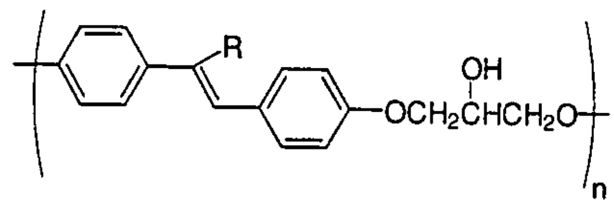
Fuel barrier polymers which can be employed in the practice of the present invention for preparing the multilayer laminate structure have a Fuel CM15 permeability of 45 g-mil/m^2-day or less, based on a layer thickness of 1 mil, when measured at 40°C and under ambient pressure conditions of 700 to 760 torr.

These fuel barrier polymers include hydroxy-functionalized polyethers, polycarbonates, polyesters or polyestercarbonates containing a moiety represented by the structure



wherein R is methyl, ethyl or propyl.

Preferably, the hydroxy-functionalized polyether containing an α-alkylstilbene moiety employed in the practice of the present invention is represented by the structure:



wherein R is methyl, ethyl or propyl and n is an integer from 10 to 1000.

The hydroxy-functionalized polyether containing an α-alkylstilbene moiety is prepared by (a) reacting an inertly-substituted or unsubstituted dihydroxy-α-alkylstilbene with the diglycidyl ether of an inertly-substituted or unsubstituted dihydroxy-α-alkylstilbene. This polymer is described in U.S. Patent 5,686,551.

Preferably, the polycarbonate, polyester, or polyestercarbonate containing the α-alkylstilbene moiety employed in the practice of the present invention comprises repeat units of the formula:

$$\{R\text{-}O\text{-}X\text{-}O\}$$

wherein R independently in each occurrence is the divalent nucleus of a difunctional aromatic diol; X is selected from:

-C(O)-, -C(O)-R^1-C(O)-, or a mixture thereof; and R^1 independently in each occurrence is the divalent nucleus of an aromatic dicarboxylic acid.

The polycarbonate, polyester, and polyestercarbonate containing the α-alkylstilbene moiety employed in the practice of the present invention are described in U.S. Patent 5,614,599.

Thermoplastic polyesters and blends thereof, and polyacetal which have a Fuel CM15 permeability of 45 g-mil/m^2-day or less, based on a layer thickness of 1 mil, when measured at 40°C and under ambient pressure conditions of 700 to 760 torr can also be employed as fuel barrier polymers in the practice of the present invention.

Preferably, the thermoplastic polyesters contain a terephthalate moiety or a 2,6-naphthalenedicarboxylate moiety.

Examples of thermoplastic polyesters which can be employed in the practice of the present invention include poly(butylene-2,6-naphthalenedicarboxylate) (PBN), poly(ethylene-2,6-naphthalenedicarboxylate) (PEN), poly(ethylene terephthalate) (PET), poly(propane terephthalate) (PPT), poly(butylene terephthalate) (PBT), and mixtures thereof. Surprisingly, it has been found that PBT, while only a marginally acceptable fuel barrier material

alone, becomes an exceptional fuel barrier material when blended with PET, which alone is a very poor fuel barrier material.

PEN and PBN and methods for their preparation (including the specific monomers employed in their formation, their proportions, polymerization temperatures, catalysts and other conditions) are known in the art and reference is made thereto for the purposes of this invention. For purposes of illustration and not limitation, reference is particularly made to U.S. Patent 5,102,705. PPT is available from Shell Chemical. PET, PBT, and polyacetal are commercially available.

Fillers having high aspect ratios can also be blended with the fuel barrier polymers. It has been found that fillers having a high aspect ratio significantly improve the fuel barrier properties of the fuel barrier polymer, while those that have low aspect ratios do not. As used herein, the term "high aspect ratio" refers to the ratio of the length or width of the platelet to the depth of the platelet which is 10 to 1000. Overall the length and width of the platelets are, each individually, from 10 to 1000 nm.

Fillers having high aspect ratios which can be employed in the practice of the present invention include, but are not limited to Mica and montmorillonite clay.

Toughening agents can also be blended with the fuel barrier polymer. Toughening agents which can be employed in the practice of the present invention include an elastomer commercially available as Paraloid®, a product of Rohm and Haas) and having a rubbery core of butyl acrylate or butadiene and a hard shell of polymethyl methacrylate, and a maleic anhydride grafted polyethylene elastomer (ENGAGE®-g-MA, a product of DuPont Dow Elastomers L.L.C.). The maleic anhydride grafted polyethylene elastomers are described in U.S. Patent 5,686,551.

The toughening agents and fillers may be incorporated into the fuel barrier polymers by using conventional melt processing, as well as dry blending techniques for thermally sensitive polymers.

The tie layer, also commonly referred to as an adhesive layer, which can be employed in the practice of the present invention is made of an adhesive material, such as a modified polyethylene elastomer. Preferably, the adhesive material is a maleic anhydride grafted polyethylene or polypropylene such as ADMER™ (trademark of Mitsui Petrochemicals) adhesive resin or ethylene-vinyl acetate copolymer resins such as ELVAX™ (trademark of DuPont).

Each of the polymers forming the layers of the multilayer laminate structure of the present invention may contain various additives in an amount that does not adversely affect the desired properties of the polymers. Examples of such additives include antioxidants, ultraviolet light absorbers, thermal processing stabilizers, colorants, lubricants, flame retardants, impact modifiers, plasticizers, antistatic agents, pigments, and nucleating agents and fillers, such as zeolite, talc, and calcium carbonate. The method of incorporating the additives is not critical. The additives can conveniently be added to the polymer prior to preparing the multilayer laminate structure. If the polymer is prepared in solid form, the additives can be added to the melt prior to preparing the multilayer laminate structure.

Processes for forming and using multilayer structures such as those described above inherently produce a certain amount of scrap material. From an economic standpoint, it is desirable to employ this scrap material in a useful manner. Generally, the scrap material is ground into particles or powder and, optionally, melted, kneaded and formed into pellets. The ground scrap material, in the form of powder, particles or pellets, may be added either as a part of the material forming one or more of the plurality of layers or as a material for forming an additional layer substantially completely made of the scrap material. Thus, the multilayer laminate structure of the present invention can comprise a further layer of a regrind (ground scrap) of the polyolefin polymer layer, the fuel barrier polymer layer and, optionally, the adhesive polymer layer.

The designed thickness of each layer in the laminate structure is dependent on a number of factors including the intended use, materials stored in the container, the length of storage prior to use, and the specific composition employed in each layer of the laminate.

In general, the laminate structure will have a total thickness of from 10 to 750 mils, preferably from 100 to 500 mils; with the thickness of the fuel barrier polymer layer(s) being from 0.1 to 50 mils, preferably from 0.5 to 25 mils; the thickness of the polyethylene layer(s) being from 9.9 to 749.9 mils, preferably from 9.9 to 499.5 mils; optionally, the thickness of the tie layer(s) being from 0.1 to 20 mils, preferably from 0.1 to 5 mils; and optionally, a regrind layer consisting of a blend of the fuel barrier polymer, polyethylene, and optionally, a tie material, from 1 to 375 mils, and preferably from 5 to 250 mils.

In a first configuration of layers, the multilayer laminate structure of the present invention comprises (A) an inner layer of a fuel barrier polymer selected from: (1) a hydroxy-functionalized polyether containing an α-alkylstilbene moiety, (2) a polyester, polycarbonate or polyester-co-carbonate containing an α-alkylstilbene moiety, (3) polyacetal, (4) PEN, PBN,

PPT, or PBT, (5) a blend of any two or more of PEN, PET, PPT, PBN, and PBT, (6) a blend of (a) polyacetal, PEN, PPT, PBN, or PBT and (b) toughening agent A or toughening agent B, (7) a blend of (a) any two or more of PEN, PET, PBN, PPT, and PBT, and (b) toughening agent A or toughening agent B, (8) a blend of (a) polyacetal, PEN, PPT, PBN, or PBT, and (b) Mica or a montmorillonite clay, (9) a blend of (a) any two or more of PEN, PET, PPT, PBN, and PBT, and (b) Mica or a montmorillonite clay, (10) a blend of (a) polyacetal, PEN, PBN, PPT, or PBT, (b) toughening agent A or toughening agent B, and (c) Mica or a montmorillonite clay, and (11) a blend of (a) any 2 or more of PEN, PET, PPT, PBN, and PBT, (b) toughening agent A or toughening agent B, and (c) Mica or a montmorillonite clay; (B) an outer layer of HDPE; (C) a tie layer of a modified polyethylene elastomer interposed between the fuel barrier polymer and the HDPE layer; and, optionally (D) a regrind layer comprising a blend of layers (A), (B), and (C) interposed between the tie layer and the outer polyethylene layer, wherein toughening agent A is a maleic anhydride-grafted polyethylene elastomer, available from DuPont Dow Elastomers L.L.C. as Engage®-g-MA, toughening agent B is an elastomer having a rubbery core (butyl acrylate or butadiene) and a hard shell, commercially available from Rohm and Haas as Paraloid®, and Mica is a high-aspect ratio inert filler, a product of Franklin Industrial Minerals.

Preferably, the inner layer is from 0.1 to 25 weight percent of the container and the outer layer is from 5.0 to 99.89 weight percent of the container. The tie layer between the fuel barrier polymer layer and the polyethylene layer is from 0.01 to 10 weight percent of the container. The optional regrind layer between the tie layer and the outer layer is from 5 to 60 weight percent of the container.

A second configuration of layers of the multilayer laminate structure of the present invention is the same as the first configuration, except the fuel barrier layer is the outer layer and the HDPE layer is the inner layer.

In a third configuration, the multilayer laminate structure of the present invention comprises (A) inner and outer layers of a fuel barrier polymer selected from: (1) a hydroxy-functionalized polyether containing an α-alkylstilbene moiety, (2) a polyester, polycarbonate or polyester-co-carbonate containing an α-alkylstilbene moiety, (3) polyacetal, (4) PEN, PBN, PPT, or PBT, (5) a blend of any two or more of PEN, PET, PPT, PBN, and PBT, (6) a blend of (a) polyacetal, PEN, PPT, PBN, or PBT, and (b) toughening agent A or toughening agent B, (7) a blend of (a) any two or more of PEN, PET, PPT, PBN, and PBT, and (b) toughening agent A or toughening agent B, (8) a blend of (a) polyacetal, PEN, PPT, PBN, or PBT, and (b) Mica or a

montmorillonite clay, (9) a blend of (a) any two or more of PEN, PET, PPT, PBN, and PBT, and (b) Mica or a montmorillonite clay, (10) a blend of (a) polyacetal, PEN, PBN, PPT, or PBT, (b) toughening agent A or toughening agent B, and (c) Mica or a montmorillonite clay, and (11) a blend of (a) any 2 or more of PEN, PET, PPT, PBN, and PBT, (b) toughening agent A or toughening agent B, and (c) Mica or a montmorillonite clay; (B) a core layer of HDPE; (C) a tie layer of a modified polyethylene elastomer interposed between the fuel barrier polymer layers and the HDPE layer; and optionally (D) a regrind layer comprising a blend of layers (A), (B), and (C) interposed between the tie layer and the outer polyethylene layer, wherein toughening agents A and B are as defined previously.

Preferably, the inner and outer layers, each individually, are from 0.1 to 25 weight percent of the container and the core layer is from 5.0 to 99.78 weight percent of the container. The tie layers between the fuel barrier polymer layers and the polyethylene layer is from 0.01 to 10 weight percent of the container. The optional regrind layer between a tie layer and the core layer is from 5 to 60 weight percent of the container.

In a fourth configuration, the multilayer laminate structure of the present invention comprises (A) an inner layer of polyethylene; (B) a core layer of a fuel barrier polymer selected from: (1) a hydroxy-functionalized polyether containing an α-alkylstilbene moiety, (2) a polyester, polycarbonate or polyester-co-carbonate containing an α-alkylstilbene moiety, (3) polyacetal, (4) a blend of (a) any two or more of PEN, PET, PPT, PBN, and PBT, and (b) toughening agent A or toughening agent B, (5) a blend of (a) any two or more of PEN, PET, PPT, PBN, and PBT, and (b) Mica or montmorillonite clay, and (6) a blend of EVOH and Mica or montmorillonite clay; and (C) an outer layer of a polyethylene; optionally (D) a tie layer of a modified polyethylene elastomer interposed between the fuel barrier polymer layer and the inner and outer HDPE layer; and optionally (E) a regrind layer comprising a blend of layers (A), (B), (C), and (D) interposed between the tie layer and the outer polyethylene layer, wherein toughening agents A and B are as defined previously.

Preferably, the polyethylene inner and outer layers together comprise from 5 to 60 weight percent of the container; the fuel barrier polymer layer comprises from 0.1 to 25 weight percent of the container, the tie layers between the fuel barrier polymer layer and the polyethylene layers comprise from 0.01 to 10 weight percent of the container, and the optional regrind layer between the tie layer and the outer polyethylene layer is from 5 to 60 weight percent of the container.

The multilayer laminate structure of the present invention can be produced using conventional extrusion techniques such as feedblock coextrusion, multimanifold die coextrusion, or combinations of the two, or may be produced by a laminating procedure whereby self-sustaining lamina are bonded together by applications of heat and pressure and reference is made thereto for the purposes of this invention. The volume (thickness) of each individual layer may be controlled as it is extruded. Thus, the overall thickness of the multilayer structure may be controlled to produce a film or sheet of desired thickness.

The laminate structure of the present invention can be fabricated into articles using conventional thermoplastic fabrication techniques such as compression molding, injection molding, lamellar injection molding, blow molding, extrusion, calendering and thermoforming. A typical thermoforming process comprises heating a thermoplastic sheet to its softening point and then shaping the sheet at a forming station utilizing various molds and/or vacuum or air pressure assists or plug assists. Other thermoforming techniques include solid phase pressure forming (SPPF) and the so-called scrapless forming process (SFP). For purposes of this invention, references to thermoforming techniques or thermoformable structures will include SPPF and SFP. During fabrication, the molecules of the polymer can be oriented by methods well known in the art. One such method is described in U.S. Patent 5,382,693. Orientation is also described in Plastics Engineering Handbook of the Society of the Plastics Industry, Inc., 4th Ed., p. 113-115, 182 and 183. Articles formed therefrom include containers, molded parts, and tubing. Examples of such articles include flexible and rigid containers such as tanks or bottles used for the storage of chemicals and fuels, including oxygenated fuels which contain alcohols such as methanol or ethanol, and tubing used in the transfer of chemicals and fuels, including oxygenated fuels which contain alcohols such as methanol or ethanol.

When formed into a container or tube, the inner layer of the multilayer laminate structure of the present invention is the layer which comes in contact with the fuel that is placed inside the container or tube. Thus, in the previously described configuration of layers of the multilayer laminate structure, the fuel barrier polymer layer of the multilayer laminate structure is either the layer which comes in contact with the fuel that is placed inside the container or tube, and/or the layer on the outside of the container or tube, or the layer which is sandwiched between layers of polyethylene, and, optionally, tie layers, and/or, regrind layers.

The following working examples are given to illustrate the invention and should not be construed as limiting its scope. Unless otherwise indicated, all parts and percentages are by weight.

EXAMPLES

The following are the materials and test procedures used in the examples.

Materials:

PBT: Poly(butylene terephthalate), a commercially available polyester.

PEN: Poly(ethylene-2,6-naphthalenedicarboxylate), a commercially available polyester.

PET: Poly(ethylene terephthalate), a commercially available polyester.

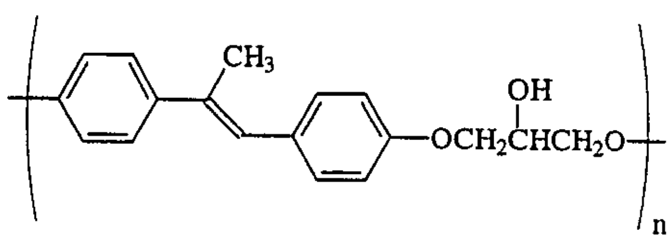
Polyacetal, a commercially available acetal resin. It is a polyoxymethylene thermoplastic polymer obtained by ionically initiated polymerization of formaldehyde + CH_2 to obtain a linear molecule of the type -O-CH_2-O-CH_2=CH_2-.

Engage®-g-MA: Graft-modified substantially linear ethylene polymers manufactured by DuPont Dow Elastomers L.L.C. and described in U.S. Patent 5,346,963.

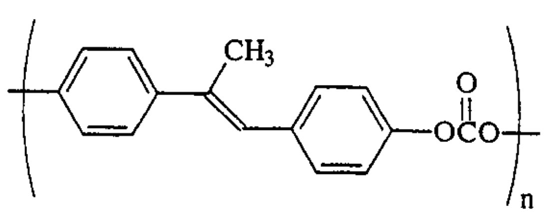
Mica: Himod 270 wet-ground Muscovite mica, a commercially available high-aspect ratio inert filler; a product of Franklin Industrial Minerals.

Eval F: An EVOH resin prepared from a monomer ratio of 32 percent by weight ethylene and 68 percent by weight vinyl alcohol; a product of Eval Co.

Hydroxy-functionalized polyether containing the α-methylstilbene moiety, represented by the structure:



Polycarbonate containing the α-methylstilbene moiety, represented by the structure:



HDPE: High density polyethylene.

Admer™ NF 500A: A modified polyethylene elastomeric adhesive, a product of Mitsui Petrochemicals.

Admer™ SF 700: A modified polyethylene elastomeric adhesive, a product of Mitsui Petrochemicals.

Admer™ SF 710: A modified polyethylene elastomeric adhesive, a product of Mitsui Petrochemicals.

Elvax 260: An ethylene vinyl acetate copolymer used as an adhesive for HDPE a product of DuPont.

Test Fuel CM15: A mixture of 42.5 percent by volume toluene, 42.5 percent isooctane and 15 percent methanol.

Test Procedures

Fuel Uptake Testing:

Pre-weighed, compression molded parts are immersed in Fuel CM15 for 14 days at 40°C to 41°C. The parts are removed from the fuel and residual liquid is removed under a strong flow of air. The parts are weighed again and the percent weight gain is calculated.

Permeation Testing:

The permeability of Fuel CM15 is measured at 40°C to 41°C using the following procedure. A compression molded, cast film extruded, or blow molded test film, in the form of a 4 inch diameter disk with a thickness between 1 and 100 mil, is mounted between the two chambers of the test cell. Fuel CM15 (95 mL) is added to the upper chamber and helium flowing at about 10 mL/minute is passed through the lower chamber. As fuel permeates through the barrier film, it is carried from the test cell and into an injector loop of a gas chromatograph (GC). At a specific frequency, the contents of the injector loop are injected onto the front end of a 25 m, 0.53 mm ID, Chrompack Poraplot U capillary column operating at 140°C using a helium flow of 10 mL/min as the carrier gas. The GC separates, identifies by retention time, and quantifies the fuel components which have permeated through the specimen film. The time since the beginning of the experiment and the identity and amount of the permeated components are stored in a computer file for further analysis.

Example 1

Several monolayer test specimens were prepared by compression molding or by injection molding. The samples (described in Table I) were evaluated for fuel uptake. The results are shown in Table I. Samples having a fuel uptake of 2 weight percent or less are considered as good barriers to fuels containing alcohols.

TABLE I

Samples	Resin or Blend	Weight Gain, percent
1	hydroxy-functionalized polyether of α-methylstilbene	2.0
2	polycarbonate of α-methylstilbene	0.7
3	HDPE	7.8
4	Eval F	2.8
5	PBT	3.0
6	polyacetal	3.0
7	PET	15.1

The data in the above table indicate that HDPE, Eval F, PET, PBT, and polyacetal do not possess good fuel barrier properties alone. PBT and polyacetal, each having a fuel uptake of 3 weight percent, are considered a marginal fuel barrier material toward fuels containing alcohols, as is Eval F.

Example 2

Several monolayer film samples (described in Table II) were prepared by compression molding. The samples were evaluated for Fuel CM15 permeability. The results are shown in Table II.

TABLE II

	Resin or Blend	Permeability*, g-mil/m²-day
8	PBT	24
9	85/15 PBT/Mica Blend	6.8
10	75/25 PBT/Mica Blend	4.2
11	75/25 PBT/Talc Blend	27.4
12	37.5/37.5/25 PBT/PET/Mica Blend	3.0
13	Eval F	50
14	75/25 Eval F/Mica Blend	7.3
15	75/25 Eval F/Talc Blend	45.7

*Permeability normalized to a thickness of 1 mil for the entire structure and measured at 41°C under ambient pressure.

As shown in Table II, common fillers such as talc, at best, only somewhat improved the fuel barrier properties of materials which, unfilled, had marginal fuel barrier properties, such as PBT and Eval F. However, fillers which had high aspect ratios, such as Mica, highly improved the fuel barrier properties of those same compounds.

Example 3

Several 3-layer laminate film samples were prepared by cast film coextrusion or by coextrusion blow molding. These laminate structures contained a fuel barrier material layer, a high-density polyethylene layer and a tie layer between the fuel barrier material layer and the polyethylene layer. In the samples prepared by cast film coextrusion, the barrier layer and the tie layer contributed approximately 10 percent and 5 percent, respectively, to the total thickness of the structure. In the coextrusion blow-molded structures, the barrier layer and the tie layer contributed approximately 24 percent and 5 percent, respectively, to the total thickness of the structure. The remaining thickness of these structures was attributed to the polyethylene layer. These films were tested for fuel CM15 permeability with the barrier material layer in direct contact with the fuel. The permeability values for these structures are based on the total thickness of these structures. The results of this testing are given in Table III.

Table III

Samples	Barrier Material	Tie Layer	Method of Fabrication	Permeability*, g-mil/m^2-day
16	50/50 PBT/PEN Blend	Admer NF-500	Cast Film Coextrusion	44
17	50/50 PBT/PEN Blend	Admer SF-710	Cast Film Coextrusion	55
18	50/50 PBT/PEN Blend	Elvax 260	Cast Film Coextrusion	66
19	PBT	Admer NF-500	Cast Film Coextrusion	104
20	PBT	Admer SF-700A	Cast Film Coextrusion	102
21	PBT	Admer SF-710A	Cast Film Coextrusion	77
22	PBT	Elvax 260	Cast Film Coextrusion	80
23	PBT	Admer SF-700A	Coextrusion Blow-molding	53
24	HDPE	Admer SF-700A	Coextrusion Blow-molding	2,670

*Permeability normalized to a thickness of 1 mil for the entire structure and measured at 41°C under ambient pressure.

As shown in Table III, the laminate structures containing PBT or 50/50 PBT/PEN as the barrier material have permeability values which are 25 to 60 times lower than a similar 3 layer structure containing 2 layers of high-density polyethylene and a tie layer between the polyethylene layers.

CLAIMS:

1. A multilayer laminate structure comprising:

(A) one or more layers of a polyolefin or a blend of two or more different polyolefins; and

(B) one or more layers of a fuel barrier polymer or blends thereof selected from:

(1) a hydroxy-functionalized polyether containing an α-alkylstilbene moiety,

(2) a polyester containing an α-alkylstilbene moiety,

(3) a polycarbonate containing an α-alkylstilbene moiety,

(4) a polyester-co-carbonate containing an α-alkylstilbene moiety,

(5) polyacetal,

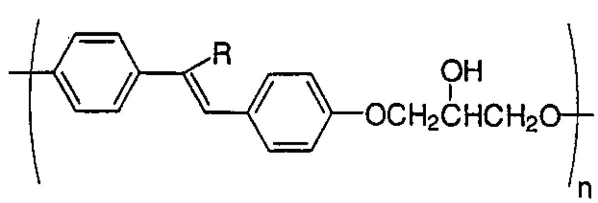
(6) blends of (1), (2), (3), (4), (5), and/or a thermoplastic polyester, and/or a toughening agent and/or a filler having a high aspect ratio, and

(7) a blend comprising (a) poly(butylene terephthalate) (PBT), (b) poly(ethylene terephthalate)(PET) and/or (c) a toughening agent and/or (d) a filler having a high aspect ratio; and, optionally

(C) a tie layer interposed between a polyolefin layer and an adjacent fuel barrier layer; and/or optionally

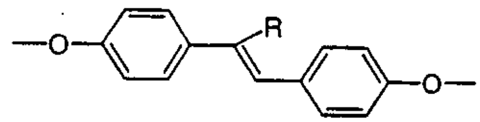
(D) a regrind layer interposed between a tie layer and a polyolefin layer.

2. The laminate structure of Claim 1 wherein the hydroxy-functionalized polyether is represented by the structure:



wherein R is methyl, ethyl or propyl and n is an integer from 10 to 1000.

3. The laminate structure of Claim 1 wherein the polycarbonate, polyester or polyester-co-carbonate contains a moiety represented by the structure



wherein R is methyl, ethyl or propyl.

4. The laminate structure of Claim 1 wherein the polyolefin is high-density polyethylene.

5. The laminate structure of Claim 4 wherein the high-density polyethylene has a density of from 0.94 to 0.99 g/cc and a melt index of from 0.01 to 35 grams per minute as determined by ASTM Test Method D-1238.

6. The laminate structure of Claim 1 wherein the tie layer is a maleic anhydride grafted polyethylene or polypropylene or an ethylene-vinyl acetate copolymer.

7. A two layer laminate structure comprising:

(A) a layer of a fuel barrier polymer selected from:

(1) a hydroxy-functionalized polyether containing an α-alkylstilbene moiety,

(2) a polyester containing an α-alkylstilbene moiety,

(3) a polycarbonate containing an α-alkylstilbene moiety,

(4) a polyester-co-carbonate containing an α-alkylstilbene moiety,

(5) poly(propane terephthalate) (PPT),

(6) poly(ethylene-2,6-naphthalenedicarboxylate) (PEN),

(7) poly(butylene-2,6-naphthalenedicarboxylate) (PBN),

(8) poly(butylene terephthalate) (PBT),

(9) polyacetal, and

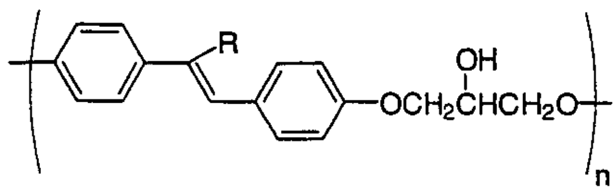
(10) blends of (1), (2), (3), (4), (5), (6), (7), (8), and/or (9), and/or PET, and/or a toughening agent and/or a filler having a high aspect ratio; and

(B) a layer of a polyolefin or a blend of two or more different polyolefins; and optionally

(C) a tie layer interposed between a polyolefin layer and an adjacent fuel barrier layer; and/or optionally

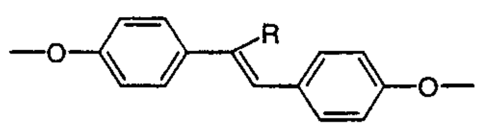
(D) a regrind layer interposed between a tie layer and a polyolefin layer.

8. The laminate structure of Claim 7 wherein the hydroxy-functionalized polyether is represented by the structure:



wherein R is methyl, ethyl or propyl and n is an integer from 10 to 1000.

9. The laminate structure of Claim 7 wherein the polycarbonate, polyester or polyester-co-carbonate contains a moiety represented by the structure



wherein R is methyl, ethyl or propyl.

10. The laminate structure of Claim 7 wherein the polyolefin is high-density polyethylene.

11. The laminate structure of Claim 10 wherein the high-density polyethylene has a density of from 0.94 to 0.99 g/cc and a melt index of from 0.01 to 35 grams per minute as determined by ASTM Test Method D-1238.

12. The laminate structure of Claim 7 wherein the tie layer is a maleic anhydride grafted polyethylene or polypropylene or an ethylene-vinyl acetate copolymer.

13. A multilayer laminate structure comprising:

(A) an inner layer of a fuel barrier polymer,

(B) an outer layer of a fuel barrier polymer,

the fuel barrier polymer being selected from:

(1) a hydroxy-functionalized polyether containing an α-alkylstilbene moiety,

(2) a polyester containing an α-alkylstilbene moiety,

(3) a polycarbonate containing an α-alkylstilbene moiety,

(4) a polyester-co-carbonate containing an α-alkylstilbene moiety,

(5) poly(propane terephthalate) (PPT),

(6) poly(ethylene-2,6-naphthalenedicarboxylate) (PEN),

(7) poly(butylene-2,6-naphthalenedicarboxylate) (PBN),

(8) poly(butylene terephthalate) (PBT),

(9) polyacetal, and

(10) blends of (1), (2), (3), (4), (5), (6), (7), (8), and/or (9), and/or PET, and/or a toughening agent and/or a filler having a high aspect ratio; and

(C) a core layer of a polyolefin or a blend of two or more different polyolefins; and optionally

(D) a tie layer interposed between a polyolefin layer and an adjacent fuel barrier layer; and/or optionally

(E) a regrind layer interposed between a tie layer and a polyolefin layer.

14. A multilayer laminate structure comprising

(A) an outer layer of a polyolefin or a blend of two or more different polyolefins; and

(B) an inner layer of a fuel barrier polymer or blends thereof, the fuel barrier polymer or blends thereof having a Fuel CM15 permeability of 45 g-mil/m^2-day or less, based on a layer thickness of 1 mil, when measured at 40°C and under ambient pressure conditions of 700 to 760 torr; and optionally

(C) a tie layer interposed between a polyolefin layer and an adjacent fuel barrier layer; and/or optionally

(D) a regrind layer interposed between a tie layer and a polyolefin layer.

15. A multilayer laminate structure comprising:

(A) an inner layer of a polyolefin or a blend of two or more different polyolefins;

(B) a core layer of a blend of EVOH and a filler having a high aspect ratio;

(C) an outer layer of a polyolefin or a blend of two or more different polyolefins; and optionally

(D) a tie layer interposed between a polyolefin layer and an adjacent fuel barrier layer; and/or optionally

(E) a regrind layer interposed between a tie layer and a polyolefin layer.

16. A multilayer laminate structure comprising

(A) an inner layer of a fuel barrier polymer selected from :

(1) a hydroxy-functionalized polyether containing an α-alkylstilbene moiety,

(2) a polyester containing an α-alkylstilbene moiety,

(3) a polycarbonate containing an α-alkylstilbene moiety,

(4) a polyester-co-carbonate containing an α-alkylstilbene moiety,

(5) polyacetal,

(6) poly(propane terephthalate) (PPT),

(7) poly(ethylene-2,6-naphthalenedicarboxylate) (PEN),

(8) poly(butylene-2,6-naphthalenedicarboxylate) (PBN),

(9) poly(butylene terephthalate) (PBT),

(10) a blend of any two or more of PEN, PET, PPT, PBN, and PBT,

(11) a blend of (a) PEN, PBN, PPT, or PBT and (b) toughening agent A or toughening agent B,

(12) a blend (a) any two or more of PEN, PET, PPT, PBN and PBT, and (b) toughening agent A or toughening agent B,

(13) a blend of (a) polyacetal, PEN, PBN, PPT, or PBT, and (b) Mica or a montmorillonite clay,

(14) a blend of (a) any two or more of PEN, PET, PPT, PBN, and PBT, and (b) Mica or a montmorillonite clay,

(15) a blend of (a) polyacetal, PEN, PPT, PBN or PBT, (b) toughening agent A or toughening agent B, and (c) Mica or a montmorillonite clay, and

(16) a blend of (a) any 2 or more of PEN, PET, PPT, PBN, and PBT, (b) toughening agent A or toughening agent B, and (c) Mica or a montmorillonite clay;

(B) an outer layer of high-density polyethylene;

(C) a tie layer of a modified polyethylene elastomer interposed between the fuel barrier polymer and the high-density polyethylene layer; and, optionally

(D) a regrind layer comprising a blend of layers (A), (B), and (C) interposed between the tie layer and the outer high-density polyethylene layer;

wherein toughening agent A is a maleic anhydride-grafted polyethylene elastomer, toughening agent B is an elastomer having a rubbery core of butyl acrylate or butadiene and a hard shell of polymethyl methacrylate, and Mica is a high-aspect ratio inert filler.

17. A multilayer laminate structure comprising:

(A) an inner layer of polyethylene;

(B) a core layer of a fuel barrier polymer selected from:

(1) a hydroxy-functionalized polyether containing an α-alkylstilbene moiety,

(2) a polyester containing an α-alkylstilbene moiety,

(3) a polycarbonate containing an α-alkylstilbene moiety,

(4) a polyester-co-carbonate containing an α-alkylstilbene moiety,

(5) polyacetal,

(6) a blend of (a) (1), (2), (3), (4), or (5) and (b) PEN, PET, PBT, PPT, or PBN, and

(7) a blend of (a) any two or more of PEN, PET, PPT, PBN, and PBT, and (b) toughening agent A or toughening agent B, and/or (c) Mica or montmorillonite clay; and

(C) an outer layer of a high-density polyethylene;

(D) tie layers of a modified polyethylene elastomer interposed between the fuel barrier polymer and the high-density polyethylene layers; and optionally

(E) a regrind layer comprising a blend of layers (A), (B), (C), and D interposed between the tie layer and the outer polyethylene layer;

wherein toughening agent A is a maleic anhydride-grafted polyethylene elastomer, toughening agent B is an elastomer having a rubbery core of butyl acrylate or butadiene and a hard shell of polymethyl methacrylate, and Mica is a high-aspect ratio inert filler.

18. A process for preparing a multilayer laminate structure which comprises coextruding:

(A) one or more layers of a polyolefin or a blend of two or more different polyolefins; and

(B) one or more layers of a fuel barrier polymer or blends thereof selected from:

(1) a hydroxy-functionalized polyether containing an α-alkylstilbene moiety,

(2) a polyester containing an α-alkylstilbene moiety,

(3) a polycarbonate containing anα-alkylstilbene moiety,

(4) polyester-co-carbonate containing an α-alkylstilbene moiety,

(5) polyacetal,

(6) blends of (1), (2), (3), (4), (5), and/or a thermoplastic polyester, and/or a toughening agent and/or a filler having a high aspect ratio, and

(7) a blend comprising (a) poly(butylene terephthalate), (b) poly(ethylene terephthalate) and/or (c) a toughening agent and/or (d) a filler having a high aspect ratio; and optionally

(C) a tie layer interposed between a polyolefin layer and an adjacent fuel barrier layer; and/or optionally

(D) a regrind layer interposed between a tie layer and a polyolefin layer.

19. A process for preparing a multilayer laminate structure which comprises coextruding:

(A) an inner layer of a fuel barrier polymer, and

(B) an outer layer of a fuel barrier polymer,

the fuel barrier polymer being selected from:

(1) a hydroxy-functionalized polyether containing an α-alkylstilbene moiety,

(2) a polyester containing an α-alkylstilbene moiety,

(3) a polycarbonate containing an α-alkylstilbene moiety,

(4) a polyester-co-carbonate containing an α-alkylstilbene moiety,

(5) poly(propane terephthalate) (PPT),

(6) poly(ethylene-2,6-naphthalenedicarboxylate) (PEN),

(7) poly(butylene-2,6-naphthalenedicarboxylate) (PBN),

(8) Poly(butylene terephthalate) (PBT),

(9) polyacetal, and

(10) blends of (2), (3), (4), (5), (6), (7), (8), and/or (9), and/or PET, and/or a toughening agent and/or a filler having a high aspect ratio; and

(C) a core layer of a polyolefin or a blend of two or more different polyolefins; and optionally

(D) a tie layer interposed between a polyolefin layer and an adjacent fuel barrier layer; and/or optionally

(E) a regrind layer interposed between a tie layer and a polyolefin layer.

20. A process for preparing a two layer laminate structure which comprises coextruding:

(A) a layer of a fuel barrier polymer selected from:

(1) a hydroxy-functionalized polyether containing an α-alkylstilbene moiety,

(2) a polyester containing an α-alkylstilbene moiety,

(3) a polycarbonate containing an α-alkylstilbene moiety,

(4) a polyester-co-carbonate containing an α-alkylstilbene moiety,

(5) poly(propane terephthalate) (PPT),

(6) poly(ethylene-2,6-naphthalenedicarboxylate) (PEN),

(7) poly(butylene-2,6-naphthalenedicarboxylate) (PBN),

(8) poly(butylene terephthalate) (PBT),

(9) polyacetal, and

(10) blends of (2), (3), (4), (5), (6), (7), (8), and/or(9), and/or PET, and/or a toughening agent and/or a filler having a high aspect ratio; and

(C) a layer of a polyolefin or a blend of two or more different polyolefins; and optionally

(D) a tie layer interposed between a polyolefin layer and an adjacent fuel barrier layer; and/or optionally

(E) a regrind layer interposed between a tie layer and a polyolefin layer.

21. A container or tube comprising the laminate structure of Claim 7 wherein the inner layer forms the inside surface of the container or tube and the outer layer forms the outside surface of the container or tube.

22. A container or tube comprising the laminate structure of Claim 14 wherein the inner layer forms the inside surface of the container or tube and the outer layer forms the outside surface of the container or tube.

23. A container or tube comprising the laminate structure of Claim 16 wherein the inner layer forms the inside surface of the container or tube and the outer layer forms the outside surface of the container or tube.

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(57) Abstract

A multilayer laminate structure comprising (A) one or more layers of a polyolefin or a blend of two or more different polyolefins; and (B) one or more layers of a fuel barrier polymer or blends thereof, the fuel barrier polymer or blends thereof having a Fuel CM15 permeability of 45 g-mil/m^2–day or less, based on a layer thickness of 1 mil, when measured at 40 °C and under ambient pressure conditions of 700 to 760 torr; and optionally (C) a tie layer interposed between a polyolefin layer and an adjacent fuel barrier layer; and/or optionally (D) a regrind layer interposed between a tie layer and a polyolefin layer.

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